

III.A.10 SOFC Compressive Seal Development at PNNL

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Objectives

- Develop cost-effective seals for solid oxide fuel cell (SOFC) stacks that offer low leak rates and desired reliability during long-term operation and thermal cycling.
- Improve understanding of degradation mechanisms affecting seal performance, including intrinsic materials degradation in SOFC environment and interactions with other SOFC components.

Approach

- Perform preliminary evaluation of seal concepts.
- Synthesize, fabricate and test seal materials and designs under SOFC-relevant conditions (atmosphere and temperature).
- Evaluate tested seal components to improve understanding of degradation processes during seal operation.

Accomplishments

- Developed a low-cost “hybrid” compressive seal based on mica paper with glass-ceramic or metallic interlayers.
- Demonstrated low leak rate and stability of hybrid seals during long-term testing with extensive thermal cycling.

Future Directions

- Develop durable, low-cost glass (glass-ceramic) seals with minimal materials/interfacial interaction/degradation and engineered interface for optimal shear strength at various sealing temperatures.
- Study interfacial reaction/degradation at various stages of operation, temperatures, and environments.

Introduction

Planar SOFC stacks require adequate seals between the interconnect and the cells in order to prevent mixing of the oxidant and fuel gases, and to prevent leaking of gases from the stack. In addition, these seals must also allow the stack to be thermally cycled repeatedly (between ambient conditions and the operating temperature). Several different approaches to sealing SOFC stacks are available, including rigid, bonded seals (e.g., glass-ceramics), compliant seals (e.g., viscous glass), and

compressive seals (e.g., mica-based composites). Rigid seals typically soften and flow slightly during stack fabrication (at a temperature above the operating temperature) but then become rigid (to avoid excessive flow or creep) when cooled to the operating temperature. The thermal expansion of rigid seals must be closely matched to the other stack components in order to avoid damaging the stack during thermal cycling. Compliant seals attempt to simultaneously perform the sealing function and prevent thermal stress generation between adjacent components. Compressive seals typically utilize

materials such as sheet-structure silicates that do not bond adjacent SOFC components; instead, the sealing material acts as a gasket, and gas-tightness is achieved by applying a compressive force to the stack. Both compliant and compressive seals potentially improve the ability of the stack to tolerate thermal expansion mismatch between the various stack components.

Recent Core Technology Program seal development work at Pacific Northwest National Laboratory (PNNL) has focused on a novel “hybrid” mica-based compressive seal concept. Initial development efforts focused on hybrid seals based on naturally cleaved Muscovite mica sheets, which offered leak rates several orders of magnitude lower than those measured with “plain” mica compressive seals. The seals, however, did not exhibit the desired thermal cycle stability, as the leak rates tended to increase with increasing thermal cycles. Microstructural characterization of cycled seals revealed undesirable degradation of the Muscovite mica due to coefficient of thermal expansion (CTE) mismatch with the mating materials. Improvements in thermal cycle stability have been obtained with seals based on Phlogopite mica paper, which has a higher “x-y (parallel to basal plane)” CTE (~ 11 ppm/ $^{\circ}$ C) than Muscovite mica (~ 7 ppm/ $^{\circ}$ C). Recent seal work has focused on optimizing Phlogopite paper-based hybrid seals to maintain low leak rates during long-term operation and thermal cycling.

Approach

Candidate seals were evaluated by studying seal quality (i.e., leak rate or open circuit voltage) as a function of temperature, gas pressure and composition, and applied compressive load. For leak rate measurements, the seals were tested with simulated stack components using a test fixture which applied the desired compressive load and then measured changes in gas pressure due to leakage. Stability and resistance to chemical interaction with other SOFC components were evaluated through thermogravimetric analysis, x-ray diffraction, electron microscopy, and optical microscopy. The hybrid seals consisted of commercially available Phlogopite mica paper sandwiched between thin layers of glass or metal. The seals were typically fabricated by inserting the mica paper between

polymer tapes (prepared by conventional tape casting techniques) which contained the glass powder, or between metal foils. Sealing was accomplished by placing the tri-layer structure between the stack component materials to be sealed.

Results

Due to space constraints, only results for hybrid Phlogopite mica seals with Ag interlayers are reported. Long-term (4000 hours) ageing and short-term cycling tests were performed. Seals were tested between an Inconel600 (2"x2") fixture and an yttria-stabilized zirconia (YSZ) electrolyte plate under a compressive stress of 12 psi. A reducing gas of $\sim 2.7\%$ H₂/balance Ar with $\sim 3\%$ H₂O was passed over the sample to simulate the SOFC anode environment. The seal was subjected to alternating periods of isothermal testing at 800°C and repeated short-term thermal cycling from $\sim 100^{\circ}$ C to 800°C, with dwells at 800°C for 2 hours for leak testing. The leak rates over the entire period of isothermal ageing, the 1st stage of thermal cycling, and the 2nd stage of thermal cycling are shown in Figures 1, 2, and 3, respectively. It is evident that the hybrid mica seal with Ag interlayers showed good thermal stability over the entire (4000 hours) period of isothermal ageing. In addition, the leak rates remained fairly stable during the two stages of short-term thermal cycling, with leak rates in the range of ~ 0.02 to ~ 0.04 sccm/cm of seal perimeter. It is interesting to note that the leak rates increased slightly to ~ 0.04 sccm/cm after the 1st stage of

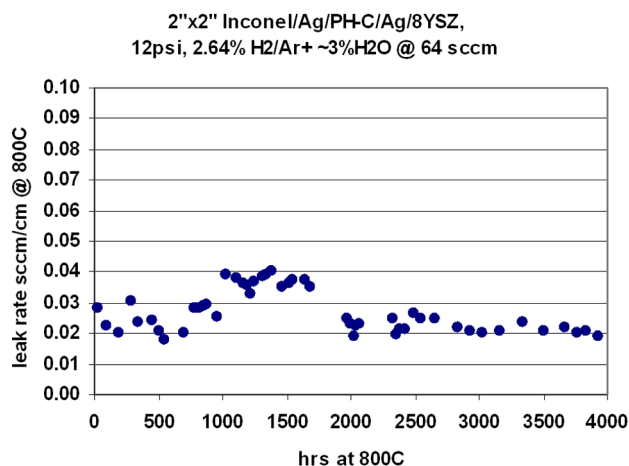


Figure 1. Leak Rate of Hybrid Phlogopite Mica Seal with Ag Interlayer: Complete Data for Ageing Tests at 800°C

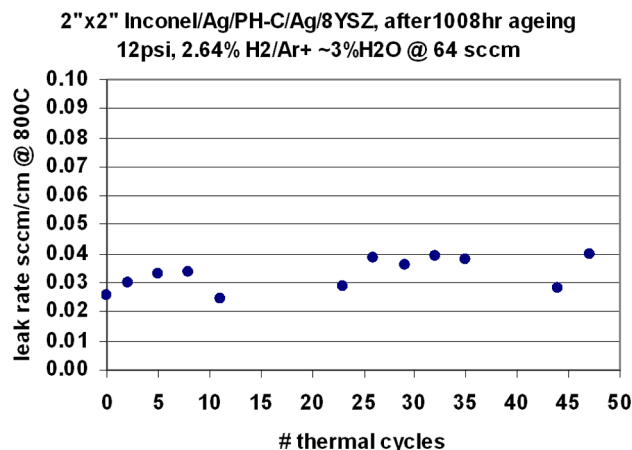


Figure 2. Leak Rate of Hybrid Phlogopite Mica Seal with Ag Interlayer: Thermal Cycling Data after Isothermal Ageing for 1008 hrs

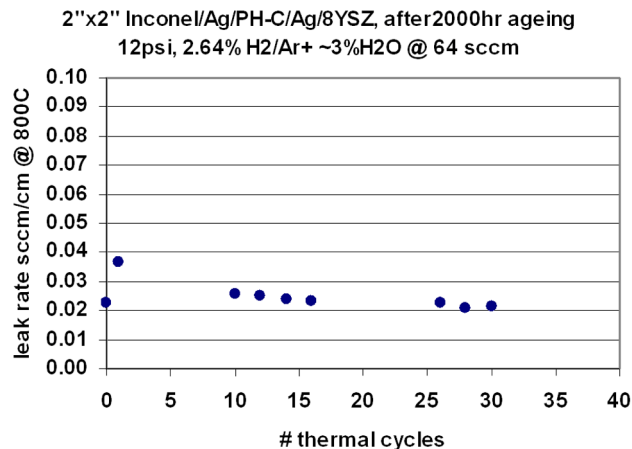


Figure 3. Leak Rate of Hybrid Phlogopite Mica Seal with Ag Interlayer: Thermal Cycling Data after Isothermal Ageing for 2000 hrs

ageing, but gradually decreased to ~0.02 sccm/cm after about 3000 hours. The current results are quite promising since the duration of this test represents ~1/10 of the desired life time (40,000 hours) for stationary SOFC applications. A leak rate of 0.02 sccm/cm would likely represent less than 1% of the total fuel flow in an actual SOFC stack.

Conclusions

Low-cost, easily fabricated “hybrid” seals based on Phlogopite mica were found to offer stable, low leak rates under relatively low applied compressive stress during isothermal and thermal cyclic exposure conditions.

FY 2005 Presentations

1. “Compressive Seal Development for Solid Oxide Fuel Cells,” Y.-S. Chou, J.W. Stevenson, and P. Singh, 6th Annual SECA Alliance Workshop, Pacific Grove, CA, April 17-22, 2005.
2. “Compressive Seal Development for Solid Oxide Fuel Cells,” Y.-S. Chou, J.W. Stevenson, and P. Singh, SECA Core Technology Program Review Meeting, Tampa, FL, January 27-28, 2005.
3. “Combined Aging and Thermal Cycling of Compressive Mica Seals for Solid Oxide Fuel Cells,” Y.-S. Chou and J.W. Stevenson, 2nd International Symposium on Solid Oxide Fuel Cell (SOFC) Materials and Technology, 29th International Conference on Advanced Ceramics and Composites (American Ceramic Society), Cocoa Beach, FL, January 23-28, 2005.
4. “Glass-Mica Composite Seals for Solid Oxide Fuel Cells,” Y.-S. Chou and J.W. Stevenson, 2nd International Symposium on Solid Oxide Fuel Cell (SOFC) Materials and Technology, 29th International Conference on Advanced Ceramics and Composites (American Ceramic Society), Cocoa Beach, FL, January 23-28, 2005.
5. “Glass-Mica Composite Seals for Solid Oxide Fuel Cells,” Y.-S. Chou and J.W. Stevenson, 2nd International Symposium on Solid Oxide Fuel Cell (SOFC) Materials and Technology, 29th International Conference on Advanced Ceramics and Composites (American Ceramic Society), Cocoa Beach, FL, January 23-28, 2005.
6. “Status of Compressive Mica Seals at PNNL: Effect of Long-term Thermal Cycling and Temperature Gradients,” Y.-S. Chou and J.W. Stevenson, 2004 Fuel Cell Seminar, San Antonio, TX, November 1-5, 2004.
7. “Compressive Mica Seals for Solid Oxide Fuel Cells,” Y.-S. Chou and J.W. Stevenson, ASM Materials Solutions Conference, Columbus, OH, October 18-20, 2004.

FY 2005 Publications

1. Y.-S. Chou and J.W. Stevenson, “Long-term Thermal Cycling of Phlogopite Mica-based Compressive Seals for Solid Oxide Fuel Cells,” *Journal of Power Sources*, 140, 340 (2005).
2. Y.-S. Chou and J.W. Stevenson, “Novel Infiltrated Phlogopite Mica Compressive Seals for Solid Oxide Fuel Cells,” *J. Power Sources*, 135, 72 (2004).

3. Y.-S. Chou and J.W. Stevenson, "Long-term Thermal Cycling of Phlogopite Mica Based Compressive Seals for Solid Oxide Fuel Cells," in *Developments in Fuel Cells and Lithium Ion Batteries* (Ceramic Transactions Volume 161), edited by Arumugan and Manthiram, p. 69, American Ceramic Society, Westerville, OH (2004).
4. Y.-S. Chou and J.W. Stevenson, "Infiltrated Phlogopite Micas with Superior Thermal Cycle Stability as Compressive Seals for Solid Oxide Fuel Cells," in *Developments in Fuel Cells and Lithium Ion Batteries* (Ceramic Transactions Volume 161), edited by Arumugan and Manthiram, p. 89, American Ceramic Society, Westerville, OH (2004).